Determination of Tungsten in Iron and Steel. I : Investigations on the Perchloric Acid Method

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Investigations on the Perchloric Acid Method*

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(Received July 18, 1950)

Synopsis

The conditions for the determination of tungsten in iron and steel have been studied by the use of perchloric acid.

Tungsten can be precipitated quantitatively with a single fuming of perchloric acid by the following treatment: the sample is dissolved in aqua regia and evaporated to the white fume after an addition of 50 ml of perchloric acid; after cooling, 30 ml of 6N hydrochloric acid is added and its final volume is brought to 150 ml with water so as to adjust the concentration of hydrochloric acid between 1～1.5N. The solution is warmed at 70°～80° C for an hour and then filtered. Applying this method also to the rapid determination, tungsten can be determined within about 20 minutes.

I. Introduction

Some methods for the determination of tungsten in iron or steel without any use of cinchonine which has an extensive use for it, have been required in some case. Particularly, it is difficult to get the reagent under the present circumstances.

The perchloric acid method(1) is one of them and it has the distinguished advantages in that sillicon can be determined together with tungsten and in that chromium and manganese can be also determined from the filtrate. But the usual prccedure is much complicated, namely, tungesten found by fuming once is so small (50%～70%) that it is impossible to determine tungsten by and, for the correct determination, or more fuming with perchloric acid should be required. So, the present authors have made studies on this method to eliminated the disadvantage and to make it easy.

II. Experimental results

1. Influences of several acids on the detemination of tungsten

Tungsten trioxide had been considered to be insoluble after a complete fuming with perchloric acid, so conditions for the dissolution of the sample (tungsten steel) and for the dilution of the solution containing the precipitate made by fuming, were investigated. A sample was dissolved with either aqua regia or perchloric acid, in the former case perchloric acid being added, and both were brought to fuming. After 15 minutes' fuming, the solution was diluted with water

* The 597th report of the Research Institute for Iron, Steel and Other Metals. This is published in the Journal of Japan Institute of Metals, 6 (1942), 391.

(1) A. Claberg and P. Behmenberg, Z. anal. Chem.104 (1936), 245.

only, or diluted with 6N hydrochloric acid, 6N sulfuric acid or 6N nitric acid and then more with water. In detail, the solution was cooled for few minutes after fuming, and 50 ml of water or 6N acid was added, and then the solution was heated slightly for 5 minutes. It was further diluted with 80 ml of water and warmed at 70~80°C for an hour. The precipitates after cooling were filtered off with a

Table 1.

Treatment*	Washing solution	Tungsten obtained(%)	Average (%)	Differences (%)
1	3% perchloric acid	1.30 1.09 1.19	1.19	−0.84
2	3% perchloric acid	1.91 1.91 1.91	1.91	−0.12
3	0.5N sulfuric acid	1.42 1.42 1.42	1.42	−0.61
4	0.5N sufuric acid	1.75 1.75 1.75	1.75	−0.28
5	0.5N nitric acid	1.75 1.75 1.75	1.75	−0.28
6	0.5N nitric acid	1.93 1.94 1.93	1.93	−0.10
7	0.5N hydrochloric acid	2.03 2.03 2.03	2.03	0.00
8	0.5N hydrochloric acid	2.04 2.03 2.03	2.03	0.00

*Treatment 1. Dissolved with 50 ml perchloric acid, fuming, diluted with 100 ml water. 70-80°C for an hour.

2. Dissolved with 50 ml aqua legia, 50 ml perchloric acid added, diluted with 100 ml water fuming, 70~80°C for an hour.
3. Dissolved with 50 ml perchloric acid, diluted with 50 ml 6N sulfuric acid and 80 ml water, 70~80°C for an hour.
4. Dissolved with 50 ml aqua regia, 50 ml perchloric acid added, fuming, diluted with 50 ml 6N sulfuric acid and 80 ml water, 70~80°C for an hour.
5. Dissolved with 50 ml perchloric acid, fuming, diluted with 50 ml 6N acid and 80 ml water, 70~80°C for an hour.
6. Dissolved with 50 ml aqua regia, 50 ml perchloric acid added, fuming, diluted with 50 ml 6N nitric acid and 80 ml water, 70~80°C for an hour.
7. Dissolved with 50 ml perchloric acid, fuming, diluted with 50 ml 6N hydrochloric acid and 80 ml water, 70~80°C for an hour.
8. Dissolved with 50 ml aqua regia, 50 ml perchloric acid added, fuming, diluted with 50 ml 6N hydrochloric acid and 80 ml water, 70~80°C for an hour.

precise filter paper and ignited to an oxide in an usual manner, and silica was

eliminated. The weighed impure tungsten trioxide was fused with sodium carbonate, and iron oxide in it was estimated to find the amount of pure tungsten trioxide. The components of the sample which was the Japan Iron and Steel Standard Sample No. 11, were as follows: C, 0.58%; Si, 0.?5%; Mn, 0.35%; P, 0.07%; S, 0.011%; Cu, 0.29%; Ni, 0.06%; Cr, 0.12%; W, 2.03%. The results obtained were shown in Table 1. As shown in Table 1, the dissolution with perchloric acid gave lower results than wich aqua regia, and it was clear that a large amount of tungsten escaped in the filtrate. And for the dilution after fuming, the best result, which coincided with the standard value, was obtained when 50 ml of 6N hydrochloric acid and then 80 cc of water were used, and the use of water only or sulfuric acid did not give good results. The use of nitric acid gave somewhat good result, but was inferior to that with hydrochloric acid.

It was clear that tungsten trioxide was made insoluble by fuming, but a large amount of tungsten might have been carried away into the filtrate by careless treatments that followed.

2. Influences of hydrochloric acid concentration

After fuming with perchloric acid, the solution was diluted with hydrochloric acid and then with water, so the concentration of hydrochloric acid in the solution should be an important factor.

The same sample was taken and dissolved with 30 ml of aqua regia, 50 ml of perchloric acid was added and the solution was kept in fuming for half an hour. Then, 50 ml of 6N hydrochloric acid was added it, and it was heated on a hot asbestos plate for five minutes and then at 70~80°C for an hour. The solution containing the precipitates was cooled and tungsten was determined in the same manner as described above. The concentration of hydrochloric acid in the solution treated thus was about 3.5 N and the results obtained were shown in Table 2. According to them, an addition of water and then heating were required, for the precipitates were dissolved little if they were diluted with the acid only.

Table 2.

Sample (g)	Impure tungsten trioxide (mg)	Ferric oxide adsorbed (mg)	Tungsten trioxide (mg)	Tungsten (%)
2.0000	46.2	3.0	43.2	1.713
	46.3	3.0	43.3	1.717
	44.8	3.2	42.6	1.688

Therefore, the amount of water to be added, namely, the hydrochloric acid concentration, was tested. Fifty milliliters or 25 ml of perchloric acid was added to the same solution of the sample and fumed weakly for half an hour, various amounts of 6N hydrochloric acid was added, and the final volume of the solution was brought to 150 ml with water and then heated at 70~80°C for an hour and then tungsten was determined in all case in the same way as above. The results obtained with 2g of the above standard sample (W = 2.03%) are shown in Table 3. As

shown in Table 3, the precipitation was almost complete in 0.5~1.8N of the acid, and it was entirely complete and no tungsten was detected in the filtrate in 1~1.5N, by fuming once with the use of 50 ml of perchloric acid. And when 25 ml

Table 3.

Perchloric acid(60%) (ml)	Hydrochloric acid(6N) (ml)	Final volume(ml) (hydrochloric acid concentration)	Tungsten trioxide found (mg)	Tungsten (%)	Tungsten trioxide from filtrate(mg)	Tungsten from filtrate(%)
50	75	150 (3N)	47.1 47.2 47.3	1.868 1.872 1.875		
50	50	150 (3N)	50.9 51.0 50.8	2.018 2.022 2.015	1.4 1.0 1.3	0.055 0.039 0.051
50	50	165 (1.8N)	51.1 51.2 51.3	2.026 2.030 2.034	1.3 0.9 1.1	0.051 0.035 0.043
50	37.5	150 (1.5N)	51.7 51.6 51.7	2.050 2.046 2.050	No ppt. from filtrate	
50	25	150 (1N)	51.6 51.5 51.7	2.046 2.042 2.050	No ppt. from filtrate	
50	12.5	150 (0.5N)	51.2 51.1 50.9	2.030 2.026 2.018	0.6 0.5 1.0	0.024 0.020 0.039
25	62.5	150 (2.5N)	50.6 50.6 50.5	2.006 2.006 2.002	1.1 1.0 1.2	0.043 0.039 0.047
25	50	150 (2N)	51.1 51.3 51.2	2.026 2.034 2.030	0.8 0.7 0.7	0.031 0.027 0.027
25	37.5	150 (1.5N)	51.1 51.0 51.2	2.026 2.022 2.030	1.1 1.0 1.0	0.043 0.039 0.039
25	25	150 (1N)	50.9 51.1 51.0	2.018 2.026 2.022	1.1 1.1 1.0	0.043 0.043 0.039
25	12.5	150 (0.5N)	48.3 47.9 48.2	1.920 1.899 1.916	3.3 4.0 3.5	0.130 0.159 0.138

of perchloric acid was used and the hydrochloric acid concentration was 1~2.5N, it was almost complete, but some of tungsten was detected in the filtrate. So the use of 50 ml of perchloric acid and fuming weakly for half an hour are desired. Though the extent of fuming have some influence on the residual amount of perchloric acid, it may be negligible if 50 ml of the acid is used. By these results it is made clear that tungsten can be determined completely if the sample is dissolved with aqua regia, then 50 ml of perchloric acid is added, and, after a weak fuming for half an hour, the solution is diluted to 150 ml in all, in which

the concentration of hydrochloric acid is 1~1.5N.

Procedure for the determination of tungsten in steel

Applying the investigations described above, a procedure for tungsten analysis of steel is outlined as follows: take 0.5~?g of sample, dissolve with 15~30 ml of 60% perchloric acid heat to fume and keep fuming weakly for half an hour. After cooling, and 30 ml of 6N hydrochloric acid, bring the solution to 150 ml with water, then warm at 70~80° for an hour and tungsten is all precipitated.

Filter the precipitates with a precise filter paper after cooling, wash it well with 0.5N hydrochloric acid, ignite it to an oxide in a platinum crucible at a temperature as low as possible and weigh it. Eliminate silica from it by the hydrochloric sulfuric acids treatment, then weigh again and the impure tungsten trioxide is obtained and silica is determined. Fuse the impure tungsten trioxide with sodium carbonate, then determine ferric oxide and chromic oxide, and grams of pure tungsten trioxide are obtained in the same way as usual. Manganese, chromium and others can be determined from the filtrate.

3. Analytical results of several samples

By the best procedure discussed above, tungsten analyses of several samples were carried out, which were high speed steel of the standard sample No.9, stellite and ferrotungsten of the standard sample No.16. The results obtained are shown in Table 4. In the high speed steel analysis, if a larger amount of the sample was taken, a trace of tungsten was found in the filtrate, but the analytical

Table 4.

Sample (tungsten content by cinchonin method)	Sample taken (g)	Tungsten trioxide found (mg)	Tungsten (%)	Tungsten trioxide found from filtrate (mg)	Tungsten from filtrate (%)
High speed steel J.S.S. No.9 (W=19.33%)	0.2000	48.9 49.0 48.9	19.39 19.43 19.39	No ppt. from filtrate	—
	0.5000	122.2 122.3 122.1	19.38 19.40 19.37	0.1 0.1 0.2	0.02 0.02 0.03
Stellite (W=15.41%)	0.3000	58.2 58.0 58.2	15.39 15.33 15.39	0.1 0.2 0.1	0.03 0.05 0.03
Ferro-tungsten J.S.S. No.16 (W=76.67)	0.5000	484.0 484.1 484.3	76.77 76.79 76.82	No ppt. from filtrate	—

results were a little higher then those by the cinchonine method. Stellite also was analysed correctly by fuming once, which contained 54.17% Co, 27.00% Cr, 0.42% Mo and 2.92% C. In the ferrotungsten analysis, the sample was dissolved with hydrofluoric and nitric acids, and the acids were expelled by perchloric acid fuming, then followed as it the others. In this case no trace of tungsten could be found in the filtrate and the result obtained was a little higher then that by

the cinchonine method.

4. On determination of chromium

The advantage of this method is that silicon can be determined at the same time, and moreover manganese and chromium can be determined from the filtrate, but there will be some danger that some of chromium will be missed as chromyl cholride when hydrochloric acid is added after fuming with perchloric acid. Especially when 6N hydrochloric acid was added to the hot perchloric acid solution, the evolution of it was observed clearly. Therefore, some investigation was made on this subject and also on whether chromium would be volatilized or not in perchloric acid fuming after dissolving the sample with aqua regia. The sample employed was a heat resistance steel, which contained 0.73% tungsten and 16.21% chromium.

Chromium content determined by the usual method after dissolving with hydrochloric or sulfuric and nitiric acids was compared with the results obtained by the following procedures. One gram of the sample was dissolved with prechloric acid or aqua regia and the solution was heated to perchloric acid fuming, and after fuming for 30 minutes it was taken off from the hot plate, and immediately or after cooling, 30 ml of 6N hydrochloric acid was added, and then it was diluted with water. Chromium adsorbed by tungsten trioxide was fused with sodium carbonate and determined colorimetrically, and it was added to the amount of chromium which was determined after the oxidation of the filtrate. The results obtained are shown in Table 5. Per cent of chromium in the case in which 6N

Table 5

Treatment	Dissolve with sulfuric acid nitric acid added	Dissolve with hydrochloric acid, nitric acid added, sulfuric acid fuming	Dissolve with perchloric acid fuming, cool, hydrochloric acid added	Dissolve with perchloric acid, fuming, hydrochloric acid added immediately to the hot.
Chromium found(%)	16.21 16.19 16.22	16.18 16.22 16.18	16.24 16.22 16.17	16.00 15.98 15.97
Chromium average (%)	16.21	16.19	16.21	15.98

hydrochloric acid was added after cooling, was coincided with the value without any use of perchloric acid, but by the addition of perchloric acid a little evolution of a nasty smell gas was experienced. On the other hand, when hydrochloric acid was added to the hot solution soon after fuming, some evolution of a brown gas was recognized and results obtained were lower. Therefore, when chromium is determined from the filtrate, a caution must be taken that hydrochloric acid ought to be added to the cold solution.

5. Rapid determination

Tungsten trioxide liberated by fuming with perchloric acid was easily soluble in sodium hydroxide, so if the tungsten preciptate was dissolved in a definite amount of soium hydroxide and the excess of it was titrated with a standard hydrcchloric acid solution, tungsten could be determined very rapidly. Procedures for that were outlined as follows.

Procedure

Take 0.5~2g of a finely chipped sample into a conical beaker, dissolve with 50 ml of perchloric acid, warmed at 70°~80°C (if the sample is insoluble, disslove with aqua regia and then perchloric acid), heat to fume and after 3 minutes fuming, add 25 ml of 6N hydrochloric acid and 80 ml of hot water. Filter the precipitates with a precise filter paper by suction, using a platinum cone, wash the precipitates 5 times with 0.1N hydrochloric acid and once with water. Transfer the precipitate and the filter paper into the last beaker, add 20 ml of 0.1N sodium hydroxide, break the paper and warm to dissolve them. Titrate the solution with 0.1N hydrochloric acid by the use of phenolphthalein as an indicator and calculate the tungsten per cent by the following formula:

$$\frac{\text{ml of 0.1N sodium hydroxide added} - \text{ml of 0.1N hydrochloric acid titrated}}{\text{grams of sample}} \times 0.9196 = \text{Tungsten \%}$$

Time required for the analysis was about 19~25 minutes.

Analytical results

Table 6.

Sample	0.1N sodium hydroxide amount added (F=0.9283) (ml)	0.1N hydrochloric acid amount titrated (F=1.0638) (ml)	0.1N sodium hydroxide consumed (F=1.0000) (ml)	Tungsten (%)
Tungsten-steel J.S.S. No.13 (W=2.03%)	20	13.25	4.47	2.06
		13.30	4.42	2.03
		13.22	4.51	2.07
		13.31	4.41	2.03
		13.22	4.51	2.07
Tool steel (W=0.74%)	20	15.89	1.67	0.77
		16.00	1.59	0.73
		15.95	1.66	0.76
Chrom Tungsten steel (W=1.37%)	20	14.60	3.04	1.40
		14.66	2.98	1.33
		14.57	3.07	1.41
Chrom Tungsten steel (W=1.80%)	20	13.62	4.08	1.88
		13.63	4.07	1.87
		13.60	4.10	1.89

Analytical results of 2g of each of several special steels by this rapid method are shown in Table 6. It shows that the method is enough to be used as a rapid method. The time required for procedures of the analysis is outlined in Table 7.

Table 7.

Procedures	Time required (min)
Weighing	1— 1
Dissolving, fuming	5— 7
Addition of hydrochloric acid and hot water	1— 1
Filtration, washing	9 -12
Dissolving, titration	3— 4
Total	19—25

6. Ignition temperature of tungsten trioxide

Tungsten trioxide may be lost by volatilization when it is ignited at a high temperature, though it may be a very little. Therefore it must be ignited at a temperature as low as possible. The authors made some investigation on the suitable condition for the ignition by gas burners. Ignitions at several degrees by some burners were carried out. The results obtained are shown in Table 8. According to the result

Table 8.

	Tungsten trioxide (mg)	Loss (mg)	Tungsten trioxide (mg)	Loss (mg)	Tungsten trioxide (mg)	Loss (mg)
Tungsten trioxide by ignition at dull red	50		50.1		49.8	0.0
Weakly by Bunsen burner for 30 min	50	0.0	50.0	0.1	49.8	0.6
Strongly by Bunsen burner for 30 min	49.4	0.6	49.4	0.6	49.2	0.4
Strongly for more 30 min by Bunsen burner	49.1	0.3	49.0	0.4	48.8	0.4
By Mecker burner for 30 min	48.7	0.4	48.5	0.5	48.4	0.4
By Mecker burner for more 30 min	48.4	0.3	48.2	0.3	48.0	0.4
Loss in sum		1.6		1.8		1.8

obtained, it is clear that correct results are obtained when it is ignited at a dull red of the bottom of a platinum crucible by Bunsen burner, even if it is ignited for a long time.

Summary

1. Procedures for tungsten analysis of steels by the perchloric acid fuming method were investigated to find the most suitable conditions.

2. Tungsten could be precipitated quantitatively and determined by only fuming once if a definite concentration of hydrochloric acid was employed in the acid treatment after perchloric acid fuming of the aqua regia solution of the sample.

3. The complete precipitation was carried out when 50 ml of perchloric acid was used, and the solution was cooled and diluted with a diluted hydrochloric acid

after 30 minutes fuming and brought to 150 ml with water to make hydrochloric acid concentration to 1~1.5N.

4. By the procedure tungsten analysis of several samples was made successfully, silicon could be determined at the same time and chromium, manganese or others were also done from the filtrate.

5. A direction for a rapid analysis capable within 20 minutes was given, applying this method.

6. Ignition loss of tungsten trioxide was investigated and some suitable conditions for the ignition were shown.